LABORATORY KINETIC STUDIES OF OH AND CO₂ RELEVANT TO UPPER ATMOSPHERIC RADIATION BALANCE

Final Report
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INTRODUCTION

This is the final report describing our efforts under NASA contract NASW-4848 "Laboratory Kinetic Studies of OH and CO_2 Relevant to Upper Atmospheric Radiative Balance". This report covers the time period beginning September 8, 1993 and ending September 7, 1996.

The purpose of this project was to quantify the rates of two processes which are crucial to our understanding of radiative energy balance in the upper atmosphere. The first process is radiative emission from vibrationally hot OH radicals following the $H + O_3$ reaction in the upper mesosphere. The importance of this process depends strongly on the OH radiative emission coefficients. Our goal was to measure the OH permanent dipole moment in excited vibrational states and to use these measurements to construct an improved OH dipole moment function and improved radiative emission coefficients. These OH dipole moment measurements were set up at Harvard University and carried out in collaboration with Professor William Klemperer. Significant progress was made on these experiments including the construction of a supersonic jet source for vibrationally excited OH radicals. Unfortunately, our efforts to transport the OH radicals into a second lower pressure vacuum chamber were not successful, and we were unable to make improved dipole moment measurements for OH.

The second key kinetic process which we attempted to quantify during this project is the rate of relaxation of bend-excited CO_2 by oxygen atoms. Since excitation of the bending vibrational mode of CO_2 is the major cooling mechanism in the upper mesosphere/lower thermosphere, the cooling rate of this region depends crucially on the rate of energy transfer out of this state. It is believed that the most efficient transfer mechanism is via atomic oxygen but the rate for this process has not been directly measured in the laboratory at appropriate temperatures and even the room tempeerature rate remains controversial.[1-3] We attempted to directly measure the relaxation rate of CO_2 (010) by oxygen atoms using the discharge flow technique.

This experiment was set up at Aerodyne Research. Again, significant progress was achieved in this experiment. A hot CO_2 source was set up, bend excited CO_2 was detected and the rate of relaxation of bend excited CO_2 by He atoms was measured. Unfortunately, the project ran out of time before the oxygen atom kinetic studies could be implemented.

RESULTS

OH Dipole Moment Measurements

The purpose of the OH experiments was to expand our knowledge of the OH dipole moment function by measuring the permanent dipole moments of OH in excited vibrational states. We produce OH in an excited vibrational state through a chemical reaction in a supersonic jet. The OH is pumped into more highly excited vibrational states using a Ti:sapphire laser and is detected using infrared fluorescence. The production of hot OH radicals allows the dipole moment in this excited state to be measured in the presence of an applied electric field by modulating the infrared fluorescence with microwave radiation which is resonant with Stark shifted rotational transitions.

The supersonic jet source was constructed and its operation was verified by the quantum state specific detection of OH* in the supersonic jet. The OH* was formed via:

$$H + O_3 \longrightarrow OH^*(v=3\text{-}9) + O_2 \tag{1}$$

This reaction is well known to produce vibrationally excited OH, however the vibrationally distribution expected with formation in a supersonic jet is not *a priori* obvious - nor is the concentration of hot radicals. To address these questions we resolved the OH infrared chemiluminescence using a diode array spectrometer. We monitored $\Delta v = 3$ and $\Delta v = 4$ emission between 10,000 cm^{-1} and 12,000 cm^{-1}. A sample spectrum is shown in Figure 1. The displayed spectrum spans ~10,000 to 10,400 cm^{-1} and clearly shows emission from three OH vibrational states: $v' = 3, 8,$ and 9. No emission was observed from any species other than OH*.

The relative intensity of the emission from the various vibrational states was used to estimate the relative populations of the vibrational states. The result of this exercise is shown in Figure 2 for two different sets of jet expansion conditions. In the first case, the carrier gas is nitrogen and in the second case we use nitrous oxide as the expansion gas. The vibrational "temperature" is very hot in both cases, but the presence of nitrous oxide promotes vibrational relaxation. This is quite a useful observation since it implies that we can control the OH vibrational distribution in the jet.

Less encouraging was the observation of a room temperature rotational distribution. Under all expansion conditions the rotational population distribution in each of the vibrational states was consistent with a room temperature Boltzmann distribution. The expansion conditions used in these experiments should cool the rotational degrees of freedom to ~10K. We concluded that the background pressure in the vacuum chamber was too high and that the rotationally cold OH* radicals were being rewarmed by collisions with background molecules. The best solution to this
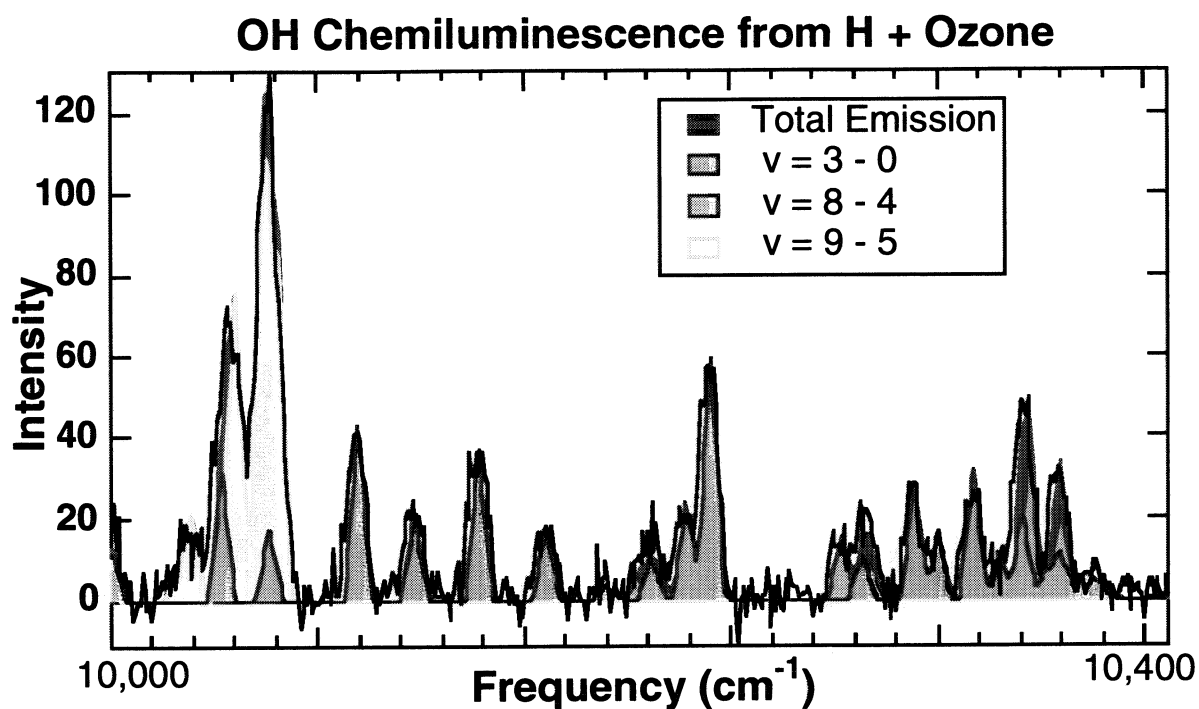
OH Chemiluminescence from H + Ozone

Figure 1 - Infrared emission spectrum from OH radicals formed in supersonic jet from the reaction of H atoms with ozone.
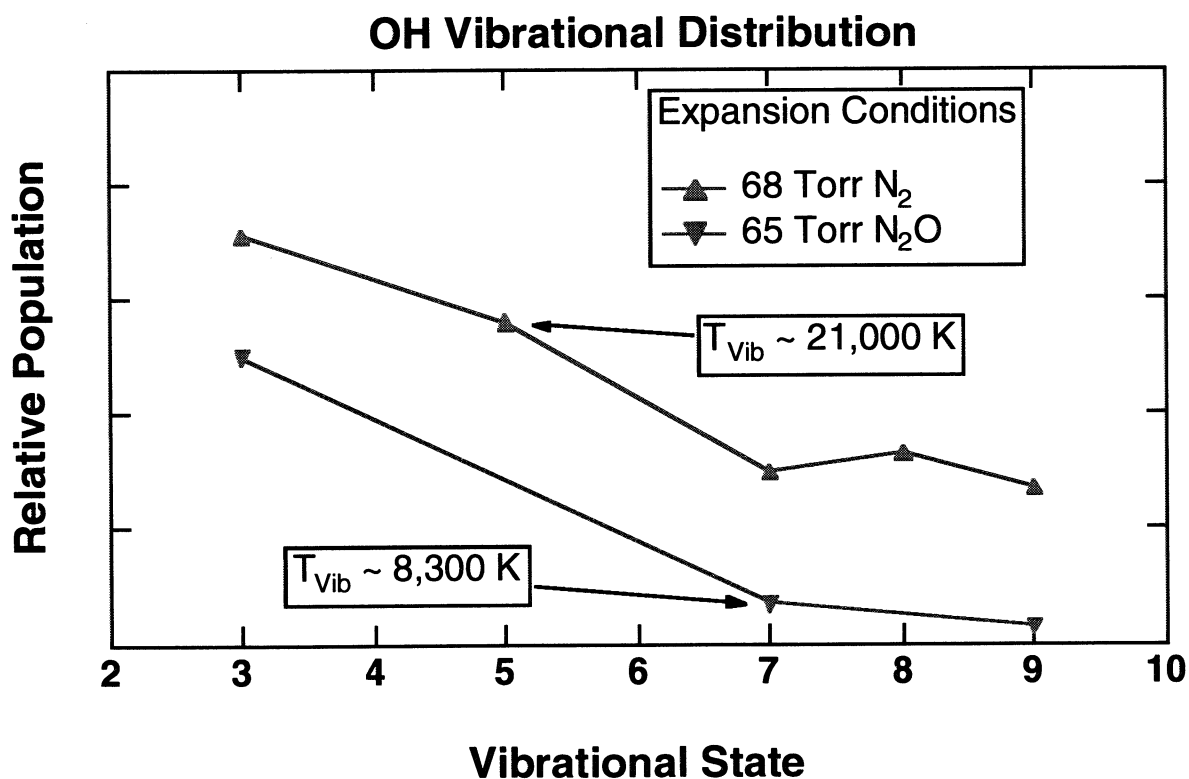
OH Vibrational Distribution

Figure 2 - Observed OH vibrational distribution as a function of jet expansion conditions.

problem was to design a dual chamber vacuum system with differential pumping employing a second large Roots blower vacuum pump.

The redesign of the vacuum system was rather involved since the vacuum chamber sits inside the Ti:sapphire laser cavity to maximize optical pumping power. This new vacuum system was constructed and installed. It appeared to work well. Unfortunately, the supersonic jet needs to be skimmed in order to transport the molecules into the low pressure chamber without reheating them. A commercial slit skimmer was purchased for this purpose. Many attempts were made to skim the supersonic jet but we were unsuccessful in our efforts. This was very frustrating since the chemiluminescent signals demonstrated that the source itself was working very well. Eventually, we resigned ourselves to this outcome and turned our attention to the second goal of this project - the vibrational relaxation of bend excited CO_2.

Vibrational Relaxation of Bend Excited CO_2

The CO_2 vibrational relaxation experiments were performed in a discharge flow apparatus. The bend excited carbon dioxide molecules are formed in a movable injector. The injector flow empties into the main flow tube mixing with a much larger flow of carrier gas (argon) and reactant (in this case atomic oxygen). By translating the injector with respect to the main flow tube, the exposure time of the bend excited CO_2 molecules can be varied. Knowledge of the flow velocity allows the calculation of a reaction rate.

The vibrationally excited carbon dioxide molecules were formed by passing them through an oven heated with a platinum filament. The oven was integrated with a quartz injector tube and could be easily translated with respect to the main flow tube. The CO_2 molecules were detected using multiple pass tunable diode laser absorption. The reactor flow passed between two astigmatic mirrors which formed a multiple pass Herriott cell. The cell was aligned to provide 360 passes of the laser beam across the flow stream. The vibrational relaxation of bend excited carbon dioxide was followed by monitoring the ratio of molecules in the excited state to those in the ground state as a function of the injector position. The population in the ground state was monitored using a line in the (001) - (000) vibrational band and the population in the bend excited state was monitored with a nearly coincident line in the (011) - (010) vibrational band. These measurements were performed at 2245.643753 and 2245.732580 cm^{-1}, respectively.

The experimental design was tested by measuring the relaxation rate of bend excited CO_2 by helium atoms. This rate has been previously measured. In the course of performing this check a significant difficulty was discovered. Translation of the carbon dioxide oven was not followed immediately by a stable concentration of bend excited CO_2. We believe that the heat emanating

from the oven significantly heated other flow tube surfaces leading to time dependent surface effects. We introduced two counter measures which helped to minimize this problem. First, we redesigned the oven to heat the CO_2 flow more efficiently, making an attempt to shield it from surrounding surfaces. Several furnace/injector designs were tried. The final and best version was a sealed double walled quartz injector (~100 cm long, 0.75 in. OD, 0.39 in. ID). On the inside of the tip of the injector, a heater wire consisting of a 0.010 in. nickel/chromium wire with a 0.040 in. Inconel sheath was coiled covering the last ~6 in. with ~20 turns. The leads to the wire extended back down the length of the inside of the injector and exited through an o-ring fitting. A 1/8 in. quartz tube with a thermocouple extended down the center of the injector to allow for temperature measurement. The inside walls of the injector were silvered to reduce radiative heat transfer from the furnace to the flow tube walls. The internal volume of the injector was evacuated to limit the convective heat transfer between the furnace and the outside wall of the injector. Second, we introduced a modulation technique to essentially measure the background relaxation rate. This technique worked by switching computer controlled solenoid valves so that the He flow was alternately switched into and out of the main flow tube. When helium was absent the signal at the detection zone was affected only by wall relaxation and carrier gas relaxation. When the He flow was present the CO_2 signal was affected by these background relaxation processes and by the process of interest - helium relaxation. The difference of these two signals gives the contribution due to the He relaxation.

This approach significantly alleviated the hysteresis in the CO_2 signal associated with the injector translation and the relaxation rate of bend excited carbon dioxide by He was determined to be (1.0 ±0.5) x 10^{-13} cm^3 mol^{-1} s^{-1}. This value is in reasonable agreement with the literature value of (1.3 ±0.1) x 10^{-13} cm^3 mol^{-1} s^{-1}.[4]

The next step in this project should have been to generate a source of oxygen atoms of known concentration. Unfortunately, the program ran out of time and funds at this point. We did generate oxygen atoms from a nitrous oxide discharge and we performed some preliminary experiments, but we have no quantitative results to report. Had we not run out of resources we would have proceeded as is described below.

Remaining Tasks for the O + CO$_2$ Relaxation Rate

The completion of this work requires the execution of two subtasks. The uncertainty of the experiment should be improved and sufficient quantities of $O(^3P)$ must be produced and quantified.

The experimental uncertainty, 50% reported (see previous section) for the relaxation rate of bend excited CO_2 by He, should be improved. The background loss, primarily due to relaxation

by collision with the flow tube wall, was in the range of 400 - 580 s^{-1}. This was higher than the anticipated background loss of ~300 s^{-1}. The maximum total first order loss in the presence of He was ~850 s^{-1}. If the fraction of the He first order losses relative to total loss could be increased, the uncertainty of the measurement should be reduced. By increasing the flow tube diameter from 1.25 cm to 3.5 cm, the wall loss would be reduced by a factor of ~8.[5] The increase in flow tube diameter should also reduce flow tube wall heating (see previous section) due to the increased wall area and carrier gas flows. A second improvement to the uncertainty of the measurement could be made by increasing the population of the bend excited CO_2. It appears as though significant relaxation is occurring due to mixing in the six way cross portion of the experiment which is where the flow tube, pumping, and multipass Herriott cell are coupled. At injector furnace temperatures of 500 C and 250 C, the population in the CO_2 bend excited state should be 30% and 16%, respectively, assuming vibrational equilibration with the furnace surface. The measured populations with the hot furnace immediately prior to the diode laser path at these temperatures were only 12% and 9%, respectively, compared to a room temperature population of the bend excited state of ~4%. The furnace temperature was maintained at 250 C for the He/CO_2 experiments in an effort to minimize the flow tube wall heating. A reduction in the volume of the six way cross should reduce the relaxation attributed to mixing in the cross. The greatest reduction is possible by filling the volume of the two arms of the cross which are not used. Additional volume reduction can be accomplished in the arm into which the flow tube enters and the arm which leads to the pump valve.

The second task which needs to be addressed is the production of ~1 x 10^{13} molecule cm^{-3} of $O(^3P)$ and the determination of the $O(^3P)$ concentration. Two different $O(^3P)$ production schemes could be used. The initially proposed scheme is the generation of $O(^3P)$ via the production of N atoms by passing N_2 through a microwave discharge and reaction of them with NO. This has proven to be a very stable oxygen atom source.[6] A second source is the production of $O(^3P)$ by passing N_2O through a microwave discharge. This source has been studied[7] extensively under conditions similar to those used in the present study and shown to produce large quantities of $O(^3P)$ with flows as high as 20 mol^{-1} s^{-1}. With carrier gas flows of ~1000 mol^{-1} s^{-1}(20 STP cm^3 s^{-1}), $O(^3P)$ concentrations of ~5 x 10^{14} molecule cm^{-3} range should be attainable. Concentrations in this range should allow for large pseudo-first order decays (250 - 3000 s^{-1}) for the range (5 x 10^{-13} - 6 x 10^{-12} cm^3 mol^{-1} s^{-1}) of the anticipated room temperature oxygen atom deactivation rate coefficient. The second source appears to be more promising of the two for production of large concentrations of $O(^3P)$ and was the source being pursued upon termination of the project.

The $O(^3P)$ concentration must be determined to measure a relaxation rate. The oxygen atoms could be monitored by vacuum ultraviolet absorption spectroscopy in which the output from an atomic oxygen resonance lamp will have a single pass across the flow tube and the light will be filtered and detected by a photomultiplier tube. This detection system could be calibrated[8] by utilizing the first $O(^3P)$ production scheme described above. A known quantity of $O(^3P)$ would be generated by production of an excess of N atoms and addition of a known quantity of NO. A second calibration which could be utilized is the titration of O atoms with NO_2 and monitoring the chemiluminescence from this reaction to determine the endpoint.[8] This would simply require an appropriate filtered photomultiplier tube which is currently in place. This could be used initially to determine the $O(^3P)$ concentrations for the experimental decays and could be replaced by the vacuum ultraviolet absorption technique described initially when deemed necessary.

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